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Microscopic Origin of Polarity in Quasi-Amorphous BaTiO₃

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The recent demonstration of pyroelectricity in quasi-amorphous thin films of BaTiO₃ introduced a new type of material: non-crystalline polar ionic solids. To elucidate the origin of polarity in this system we investigated its local bonding environment using the x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) techniques. We found that the local bonding unit of TiO₆ octahedra is identical in amorphous (as-deposited, non-polar), quasi-amorphous (non-crystalline, polar), and crystalline (highly polar) BaTiO₃. The TiO₆ octahedra are distorted due to the off-center displacement of the Ti ion; therefore, these octahedra have a local dipole moment. This implies that the macroscopic dipole moment in the quasi-amorphous films is the result of the partial alignment (<5%) of the TiO₆ octahedra.

A group from the Weizmann Institute of Science, led by Igor Lubomirsky, recently synthesized a new type of amorphous ionic solid that is polar but lacks long-range order. Radio frequency magnetron-sputtered BaTiO₃ thin films (100-180 nm) on Si (100) are pulled through a temperature gradient with a peak temperature of 600 °C. The resulting non-crystalline but pyroelectric and, therefore, polar phase was named "quasi-amorphous," in contrast to the as-deposited amorphous phase that is neither pyroelectric nor piezoelectric and, therefore, non-polar. A collaboration between Yeshiva University's Anatoly Frenkel and Lubomirsky's group investigated the origin of polarity in this new type of material. Another objective of their investigation was to find out whether the local dipoles responsible for the polarity of the quasi-amorphous BaTiO₃ had already existed in the as-deposited films, or if they were formed during the temperature-gradient step.

Ti K-edge XANES and EXAFS were the techniques of choice due to their sensitivities to the short-range ordering around Ti atoms. In addition to the as-deposited and quasi-amorphous films, we also studied the partially crystal-



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lized films prepared by isothermally annealing the as-deposited films. The XANES data features the peak A located at 4967 eV, the region corresponding to the 1s-3d transition, which is dipole-forbidden in the atom by the $\Delta L = 1$ selection rule (**Figure 1**). In order to contribute significantly to XANES data in this range of energies, the final state of the photoelectron must have some p-like character in the solid, via a hybridization of the Ti 3d and O 2p orbitals and the concomitant displacement of the Ti atom away from the TiO₆ octahedra's center of inversion symmetry.

Both the height and position of the pre-edge feature, A, are directly related to the degree of p-d mixing and, therefore, to the coordination geometry and oxidation state of Ti. The majority of Ti atoms were found to be in an octahedral environment in all samples (**Figure 2**). This result was independently confirmed by the EXAFS data (the first shell signals in all the data were identical), which implies that the local environment of the Ti⁴⁺ ion did not undergo detectable changes during the transformation of the amorphous (non-polar) phase into the quasi-amorphous (polar) phase (**Figure 3**) and that it was octahedral in both cases.

As shown by Krayzman et al, the area under the peak A is a measure of the displacement (d) of the Ti ion from the center of the TiO₆ octahedron: $A \sim d^2$. The strength of the local dipole moment is proportional to d and can therefore be measured in the XANES experiment. We obtained the values of d in all samples and found that they exceeded that of bulk BaTiO₃ (0.23 Å), the amorphous and quasi-amorphous samples being the most distorted (0.45 Å).

Preservation of the local bonding unit in amorphous BaTiO₃ implies

that the formation of the macroscopic dipole moment (polarity) in the quasi-amorphous material occurs via the partial alignment of the TiO_6 octahedra in the temperature gradient. The degree of alignment, estimated from the magnitude of the pyroelectric effect, is below 5%, which indicates that even a relatively small deviation from the random orientation of local dipoles may lead to macroscopic dipole moments, comparable to those observed in pyroelectric crystals. This was confirmed experimentally by polarized XANES measurements in quasi-amorphous films oriented

at different angles with respect to the incident x-ray beam. The anisotropy of Ti-atom displacements in the in- and out-of-film plane directions was found to be less than 5%.

The origin of polarity in quasi-amorphous BaTiO_3 is caused by 1) the existence of large off-center displacements of the Ti atoms within relatively stable TiO_6 local bonding units; 2) their weak orientational order, generated by the gradient of mechanical strain produced in the temperature gradient; and 3) the electric field resulting

from the concomitant flexoelectric effect. Therefore, the quasi-amorphous films can be viewed as being analogous to a poorly aligned nematic liquid crystal. These results imply that, under similar conditions, it may be possible to align and/or manipulate polar local bonding units (for instance, in TiO_4 , TiO_6 , NbO_4 , NbO_6 , or VO_6) to create other quasi-amorphous materials, which will similarly possess an unusual combination of properties, such as polarity in the absence of crystallinity.

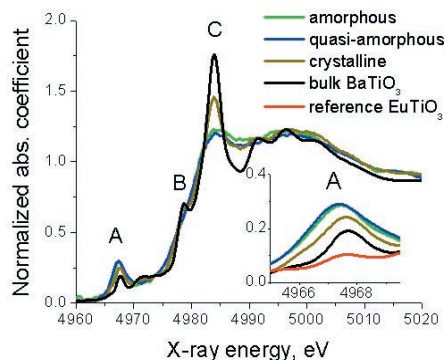


Figure 1. XANES spectra of as-deposited amorphous, quasi-amorphous, and crystalline films. The data for bulk BaTiO_3 and a sample of EuTiO_3 are given for comparison. The feature A (insert) is affected by the size of Ti displacements that range from small and dynamic (as in cubic EuTiO_3) to large and static (as in BaTiO_3).

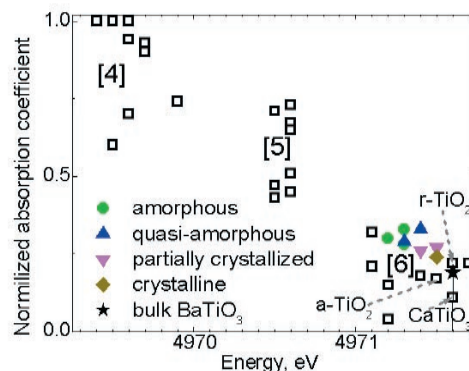


Figure 2. Intensities and positions of XANES feature A in four-, five-, and six-fold coordinated Ti in different reference compounds (hollow squares) and in our BaTiO_3 films (color symbols).

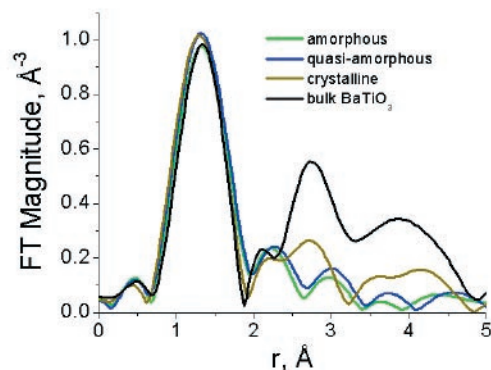


Figure 3. EXAFS data in r -space of the amorphous, quasi-amorphous, crystalline, and bulk BaTiO_3 samples.